Journal of the Taiwan Institute of Chemical Engineers 40 (2009) 518–523

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Enhancement of uranium ion flux by consecutive extraction via hollow fiber supported liquid membrane

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ARTICLE INFO

Article history:
Received 6 September 2008
Received in revised form 23 March 2009
Accepted 27 March 2009

Keywords:
Uranium
Trisodium phosphate
Liquid membrane
Hollow fiber
Synergistic extraction

ABSTRACT

The enhancement of uranium separation from trisodium phosphate, a by-product, from monazite processing through a supported liquid membrane system by a consecutive extraction using the synergistic extractants is first time demonstrated in this work. Feed solution was trisodium phosphate solution containing uranium ions of 45 ppm, and the stripping solution was nitric acid solution. The effects of types and concentrations of the extractants, concentration of HNO_3, flow rates of feed and stripping solutions and the numbers of cycles on extraction efficiency were investigated. D2EHPA, Cyanex 923, TBP, TOA and Aliquat 336 dissolved in kerosene were used as the extractants. The results showed that by using the synergistic extractant of Aliquat 336 mixed with TBP, the percentages of extraction and stripping or recovery considerably increased higher than those obtained by a single extractant. For the seventh-cycle separation by one-module operation using 0.1 M Aliquat 336 and 0.06 M TBP mixture, 0.5 M HNO_3, and equal flow rates of feed and stripping solutions at 100 mL/min, the percentages of extraction and stripping reached 99 and 53 in 350 min. The amount of uranium ions remaining in trisodium phosphate solution was 0.22 ppm, which stayed within the standard value of technical grade trisodium phosphate of 3 ppm.

1. Introduction

Monazite ore is a yellow to reddish-brown natural phosphate of the rare earths, mainly the cerium and lanthanum metals, usually with some uranium and thorium. Yttrium, calcium, iron, and silica are frequently present. The monazite processing to separate the desired rare earths for use is shown in Fig. 1, which generates a by-product, trisodium phosphate. Two grades of trisodium phosphate, a food grade and a technical grade, are extensively used. Food grade is used as an additive in cheese processing. The technical grade is for many applications, *e.g.*, in boiler-water treatment, testing of steel parts after cleaning or pickling, industrial detergents such as degreasers for steel, and heavy-duty domestic cleaners for toilets and floors (http://www.thaipoly.com). The monazite processing is composed of five essential units: 1. ore digestion unit, 2. trisodium phosphate crystallization unit, 3. dissolution unit, 4. initial precipitation unit, and 5. cerium separation unit. Monazite was digested with concentrate NaOH solution at a temperature of 140–150 °C to convert phosphate compounds of rare earths to hydroxide compounds. The hydroxide compounds of uranium, thorium and other rare earths, and a by-product trisodium phosphate were separated by filtration. Trisodium phosphate was sent to the crystallization unit, whereas the hydroxide compounds were then dissolved with HCl to remove the gangue and undigested components. The uranium and thorium in chloride solution were selectively precipitated with NaOH solution at pH 4.5–5.0 and the remaining mixed rare earths were all precipitated into mixed hydroxide cake at pH 11. Cerium in mixed hydroxide cake was later separated by leaching with HNO_3 (Suanmamuang and Laoharochanapan, 2002). Unfortunately, uranium has high solubility in water, therefore, filtration is not a suitable technique to separate uranium from trisodium phosphate solution, and it contaminates in the crystal of trisodium phosphate. The contaminated uranium is traditionally separated from trisodium phosphate solution by either ion-exchange or chemical precipitation. In general, uranium is a radioactive element which is useful at the front and back ends of the nuclear fuel cycle. However, uranium is known to cause serious environmental damage and acute toxicological effects in mammals, and its compound are potential carcinogens (Agency for Toxic Substances and Disease Registry, 2000; Clayton and Clayton, 1994). Due to safety and economic considerations, therefore, finding a new method to

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doi:10.1016/j.jtice.2009.03.010

Nomenclature

$C_{f,in}$	concentration of inlet feed (ppm)
$C_{f,out}$	concentration of outlet feed (ppm)
$C_{s,out}$	concentration of outlet striping solution (ppm)
NR_4Cl	basic extractant (Aliquat 336: quaternary amine)

separate uranium from either monazite processing directly or from trisodium phosphate is of interest among the researchers. In this work, trisodium phosphate crystal was obtained from the Rare Earth Research and Development Center, Office of Atoms for Peace, Bangkok, Thailand. Trisodium phosphate solution contains mainly uranium ions of about 45 ppm, higher than the legislation of trisodium phosphate technical grade, and a trace of rare earths.

In recent years, the separation of ions with very low concentration has been focused on liquid membrane (LM) techniques. Especially, the hollow fiber supported liquid membrane (HFSLM) is excellent to extract ions in highly-diluted solution at part per trillion (ppt) concentration levels. LMs can carry out simultaneous extraction and stripping processes in the same stage, and it benefits a non-equilibrium mass transfer and up-hill effect, where the solute can move from low-to-high concentration solutions (Franken, 1997; Gu, 2003; Sastre *et al.*, 1998; Zhang *et al.*, 2006). Main types of liquid membrane systems include emulsion liquid membrane (ELM) (Li, 1968), supported liquid membrane (SLM) (Bloch and Finkelstein, 1967), bulk liquid membrane (BLM), flowing liquid membrane (FLM) (Teramoto *et al.*, 1989) and electrostatic pseudo liquid membrane (EPLM) (Gu, 2003). The liquid membrane acts as a solvent for a transported solute which is governed by the solubility in the liquid membrane. The most interesting case arises when this solubility is controlled by a chemical reaction between the transported solute and the extractant-carrier molecule to form a solute-carrier complex. This kind of transport is called *facilitated transport* or *carrier-mediated transport* (Boyadzhiev and Lazarova, 1994). The carrier-mediated transport through an organic membrane is used largely for the separation objectives (Araki and Tsukube, 1990; Noble and Way, 1987). The selectivity in this technique is controlled by both the extraction/back-extraction equilibrium at the interfaces and the kinetics of the transported species under a non-equilibrium mass transfer process (Yang and Fane, 1999). Acidic ligands are frequently used as the extractant-carriers for separation of metal ions (Bromberg *et al.*, 1992; Juang, 1993; Kondo *et al.*, 2002; Yamini *et al.*, 2002). One of the most important advantages of such systems is the possibility to tune the selectivity and efficiency of the transport by controlling the pH of the aqueous feed phase and/or receiving phase or recovery phase (a stripping phase). The potential advantages of LM techniques over traditional separation techniques and solid membrane technique are low capital and operating costs, low energy and extractant consumption, and high fluxes. The work of Merceddes and Jose (2001) reported a transportation of niobium (V) using TBP-Alamine 336 supported liquid membrane and the work of Maysa for uranium extraction using Alquat 336 by a liquid emulsion membrane process (Maysa, 2003).

The hollow fiber supported liquid membrane (HFSLM) provides a large surface area per volume and also integrates the advantages of fiber membrane extraction process, liquid film permeation process and other liquid membrane systems (Patthaveekongka *et al.*, 2006; Ramakul *et al.*, 2004, 2005; Ren *et al.*, 2006; Zhang *et al.*, 2006). Our group also presented good results of using HFSLM, for example, a selective separation of cerium (IV), tetravalent and trivalent lanthanide ions (Pancharoen *et al.*, 2005) and the separation of uranium ions from nitrate media (Ramakul *et al.*, 2007). For the latter, the percentages of extraction and stripping were highly dependent on the concentration of HNO_3 in the feed solution and did not increase much because the permeabilities decreased due to membrane fouling concentration polarlization and the decrease in diffusivity of feed solution. In addition, Fontàs *et al.* (2000) reported that their HSLM system could be effectively used for the preconcentration of Rh(III) from diluted solutions and thus the possibility to apply it in the analysis of this metal at low level concentrations. However, HFSLM has some disadvantages primarily due to the lack of their long-time stability and larger membrane resistance. In addition, its separation efficiency and recovery depends on a proper selection of the suitable extractant in the system, and the accumulation of extracted species in the configuration of hollow fiber module.

In this work, to separate the contaminated uranium from trisodium phosphate solution to meet the legislation amount of trisodium phosphate technical grade, the consecutive extraction via HFSLM was used to enhance uranium ion flux by using a single extractant and a mixture of two extractants in liquid membrane known as the synergistic extractant.

2. Theory

The hollow fiber module shown in Fig. 2(a) contains hollow fibers aligning in the horizontal and inside them the extractant is

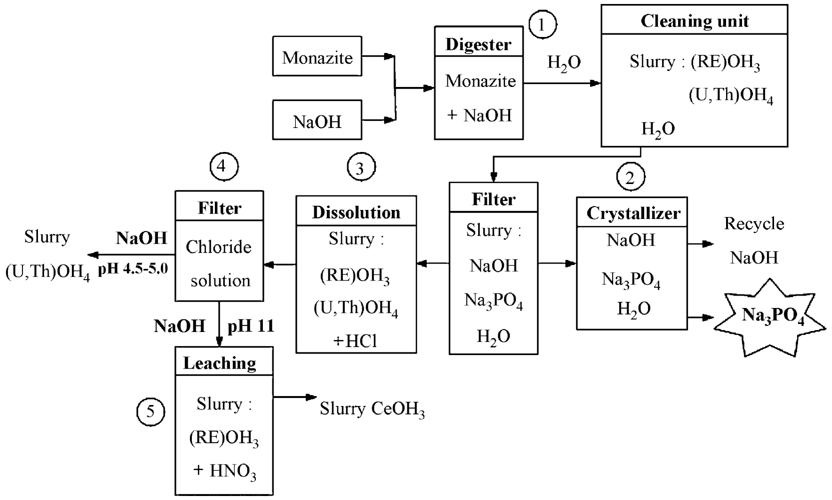

Fig. 1. Monazite processing (Suanmamuang and Laoharochanapan, 2002).